

PATENT SPECIFICATION

(11) 1 335 575

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NO DRAWINGS

- (21) Application No. 61493/70 (22) Filed 29 Dec. 1970
 (31) Convention Application No. 514 (32) Filed 15 Jan. 1970 in
 (33) Switzerland (CH)
 (44) Complete Specification published 31 Oct. 1973
 (51) International Classification C09B 23/14
 (52) Index at acceptance C4P D1Q
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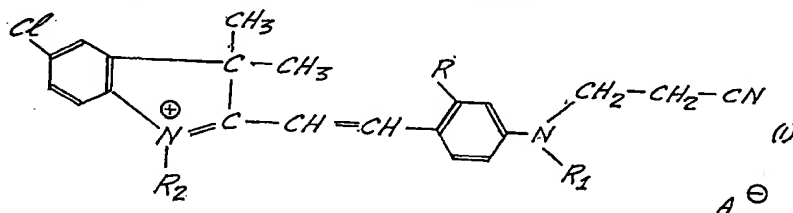


(54) BASIC STYRYL DYES FREE FROM SULPHONIC ACID GROUPS, THEIR PRODUCTION AND USE

(71) We, SANDOZ LTD., of Lichtstrasse 35, Basle, Switzerland, a Body Corporate organised according to the laws of Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to basic styryl dyes free from sulphonic acid groups which are suitable for the exhaust dyeing, pad dyeing and printing of polyacrylonitrile and acrylonitrile copolymer fibres in the form of loose fibre, yarns or textiles, and of the component of such fibres in blend yarns and fabrics.

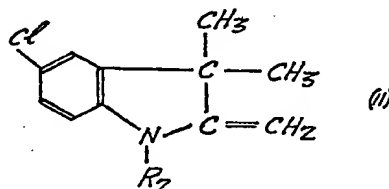
Thus, the present invention provides dyes of the formula



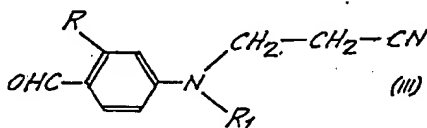
where

- R stands for a lower alkyl radical which may be substituted,
 R₁ for a straight or branched alkyl radical having at least two carbon atoms which may be substituted by a halogen atom,
 R₂ for a methyl or ethyl radical, and
 A[⊖] for an anion.

A new dye of formula (I) can be produced by the reaction of a compound of the formula



wherein R₂ is as defined above, with a compound of the formula



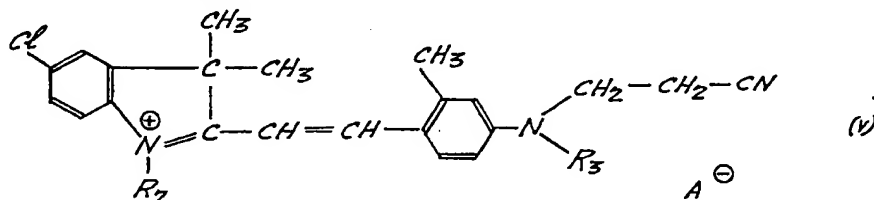
where R and R₁ are as defined above, and with an acid of the formula



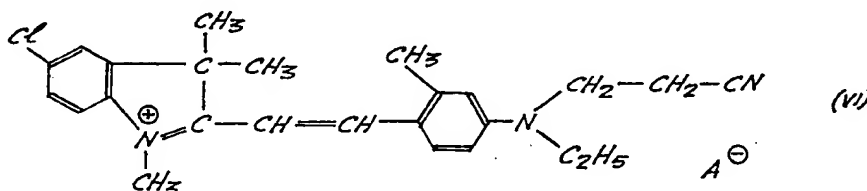
[Price 25p]

The reaction of a compound of formula (II) with a compound of formula (III) can be carried out in the presence of an acid of formula (IV), for example in water, or alternatively the reaction product of the compounds of formula (II) and (III) can be treated subsequently with an acid of this formula.

The invention provides, in particular, dyes of good quality of the formula

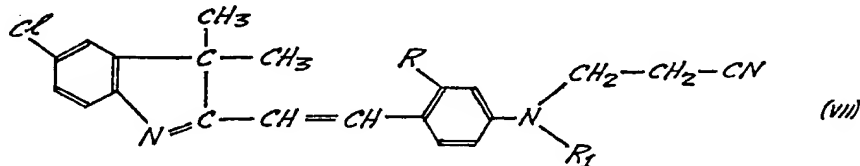


where R_2 is as defined above and R_3 stands for an ethyl, propyl or butyl radical, and more particularly dyes of the formula,



where A^\ominus is as defined above.

A further method of producing a dye of formula (I) is to methylate or ethylate, e.g. with dimethyl- or diethyl sulphate, a compound of the formula



where R and R_1 are as defined above.

The dyes of this invention can be employed for exhaust dyeing, for pad dyeing, and for printing polyacrylonitrile and acrylonitrile copolymer fibres, which may be present in loose form, or may be made up into yarns, or textiles, or may be present as a component of blend yarns or fabrics.

In addition these new dyes can be used for exhaust dyeing, pad dyeing and printing synthetic polyamide or polyester fibres which have been modified by the introduction of acid groups in manufacture. Polyamide fibres of this type are disclosed in Belgian Patent 706,104, while the corresponding polyester fibres are described in United States Patents 3,018,272 and 3,379,723. Such fibres may be present in loose form, as yarn or textiles made thereof, or as a component of blend yarns or fabrics. The dyes can also be used for the colouration of plastics materials, and the dyeing or printing of leather and paper.

The standard practice is to dye from an aqueous medium of neutral or acid reaction in a temperature range of 60–100°C, or at temperatures above 100°C under static pressure. Under these conditions the dyes are found to give level dyeings without the assistance of retarders.

It has been found that mixtures of two or more of the new dyes and mixtures of these with other cationic dyes can be employed with a high degree of success, that is to say, the dyes show good compatibility in combined application. Dyeings obtained on polyacrylonitrile and acrylonitrile copolymer fibres have good light fastness and good wet fastness properties, e.g. fastness to washing, water, sea water, cross dyeing, steam, dry cleaning, perspiration and solvents, along with good fastness to sublimation, pleating, decatizing and pressing. Some of the dyes are very soluble, especially in water, and show good compatibility with salt, good pH-stability and good resistance to prolonged boiling. Fibres other than the aforesaid, such as natural and unmodified synthetic polyamide fibres, are not dyed.

The dyes of this invention can be converted into solid or liquid dyeing preparations using standard methods, for example grinding, granulation, or dissolving in suitable solvents, if necessary with the addition of an assistant such as a stabilizer.

The term "halogen" refers to bromine, fluorine, iodine or more preferably chlorine. The lower alkyl radicals may either be straight or branched, and contain 1 to 6 or preferably 1 to 4 carbon atoms, and if they are substituted they may contain in particular one or more halogen atoms, hydroxyl or cyano groups, or aryl radicals such as phenyl radicals.

The aryl radicals are preferably phenyl radicals, which may be substituted, for example by one or more halogen atoms, nitro, amino, cyano, hydroxyl, alkyl, alkoxy, trifluoroalkyl or trichloroalkyl groups. Any alkoxy radicals present may contain 1, 2 or 3 carbon atoms.

The anion A^{\ominus} in the dyes of formula (I) may if desired be exchanged for another anion, for example with the aid of an ion exchanger or by reaction with a salt or acid, if necessary in more than one step, e.g. via the hydroxide or bicarbonate.

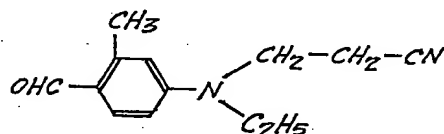
The anion A^{\ominus} may represent an organic or inorganic ion, e.g. a halide ion such as the chloride, bromide or iodide ion, or the sulphate, disulphate, methylsulphate, aminosulphate, perchlorate, carbonate, bicarbonate, phosphate, phosphoro molybdate, phosphoro tungstate, phosphoro tungstic molybdate, benzenesulphonate, naphthalenesulphonate, 4-chlorobenzenesulphonate, 4-methylbenzenesulphonate, oxalate, maleate, acetate, propionate, succinate, chloroacetate, tartrate, methanesulphonate or benzoate ion; or alternatively A^{\ominus} may represent a complex anion such as that of the zinc chloride double salts.

The reaction of a compound of formula (II) with a compound of formula (III) is preferably carried out in an organic solvent such as acetic acid in a temperature range of 50°C to 130°C, the optimum range being 70—100°C. The reaction can, however, be effected in a mixture of water and an organic solvent and in the presence of a mineral acid.

In the following Examples the parts and percentages are by weight and the temperatures are given in degrees centigrade.

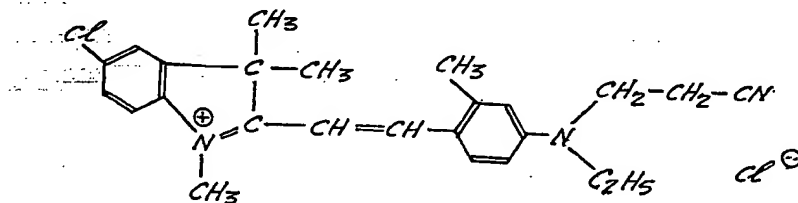
Example 1.

208 Parts of 5-chloro-1,3,3-trimethyl-2-methylene indoline (the Fischer chlorine base, prepared as given by G. Plancher in *Berichte* 31, 1496—97 (1898)) are stirred into 150 parts of acetic acid and 100 parts of water. 266 Parts of the aldehyde of the formula



(produced from the corresponding m-toluidine derivative after E. Compaigne and W. L. Archer, *J. Am. Chem. Soc.* 75, 991 (1963)) are added. The mixture is raised to 70—80° and stirred for 3 hours at this temperature, after which 1000 parts of water, 10 parts of filter earth and 6 parts of activated carbon are added. Stirring is continued for 1 hour, then the reaction mixture is filtered.

The dye of the formula

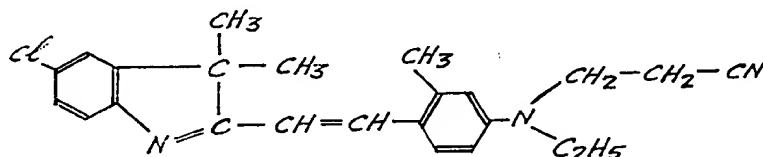


is isolated from the filtrate by one of the standard methods, such as precipitation with sodium chloride.

The dye is soluble in water and gives dyeings of bluish red shade on polyacrylonitrile and acrylonitrile copolymer fibres which have good light and wet fastness properties.

Example 1a.

The dye of Example 1 can also be produced by reacting a compound of the formula

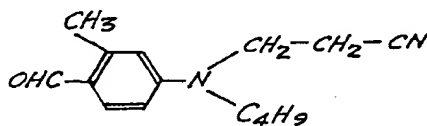


5 with dimethyl sulphate at temperatures in the range of 30° to 100°, preferably at 50—70°C, and if necessary in the presence of a solvent, and converting the resultant sulphate to the chloride by precipitation with sodium chloride. The styryl compound used in this Example can be prepared by condensation of the aldehyde used in

10 This alternative procedure can also be employed to synthesize virtually all the dyes described in the following Examples 2 to 13.

Example 2.

The aldehyde used in Example 1 is replaced by the equivalent amount of an aldehyde of the formula



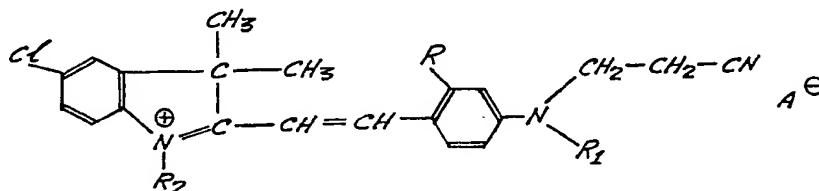
and the reaction carried out in conformity with that Example to yield a dye of comparably good quality which, like the former, gives bluish red dyeings of good fastness on polyacrylonitrile and acrylonitrile copolymer fibres.

Dyeing Example

20 A mixture of 20 parts of the dye of Example 1 and 80 parts of dextrin is ground in a ball mill for 48 hours to form a dyeing preparation. One part of this is pasted with 1 part of 40% acetic acid, and 400 parts of distilled water at 60° are run over the paste with thorough stirring. After boiling for a short time a solution is formed which is diluted with 7600 parts of distilled water and set for dyeing with 2 parts of glacial acetic acid.

25 100 Parts of a fabric of polyacrylonitrile fibre are pretreated for 10—15 minutes at 60° in a bath of 8000 parts of water and 2 parts of glacial acetic acid. The fabric is then entered into the dyebath as above at 60°, the bath is raised to 100° in 30 minutes and the fabric dyed for 1 hour at this temperature. On removal it is rinsed and dried. A level bluish red dyeing is obtained which has good light and wet fastness properties.

30 The structural composition of further dyes is shown in the following table. These dyes can be produced by the procedure of Example 1 and correspond to the formula



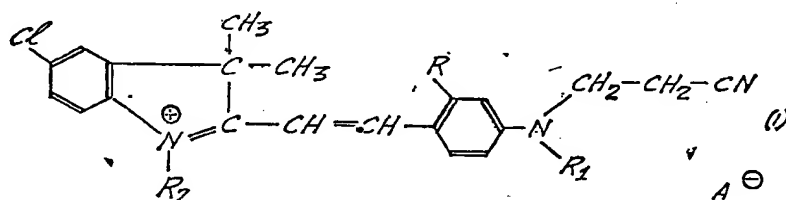
35 where R, R₁, R₂, and R' have the meanings given in the table. The anion A[⊖] may be any one of those named in the foregoing description.

TABLE

Exmp. No.	R	R ₁	R ₂	Shade of dyeing on polyacrylonitrile fibre
3	-CH ₃	-C ₃ H ₇	-CH ₃	blush red
4	do.	-CH ₂ -CH(CH ₃) ₂	do.	do.
5	-C ₂ H ₅	-C ₂ H ₅	-CH ₃	do.
6	do.	-C ₃ H ₇	do.	do.
7	do.	-C ₄ H ₉	do.	do.
8	-CH ₃	-C ₂ H ₅	-C ₂ H ₅	do.
9	do.	-C ₄ H ₉	do.	do.
10	-C ₂ H ₅	-C ₂ H ₅	-C ₂ H ₅	do.
11	do.	-C ₂ H ₄ Cl	-CH ₃	do.
12	do.	do.	do.	do.
13	-CH ₃	do.	-C ₂ H ₅	do.

WHAT WE CLAIM IS:—

1. Basic styryl dyes free from sulphonic acid groups which are of the formula



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where

R stands for a lower alkyl radical which may be substituted,

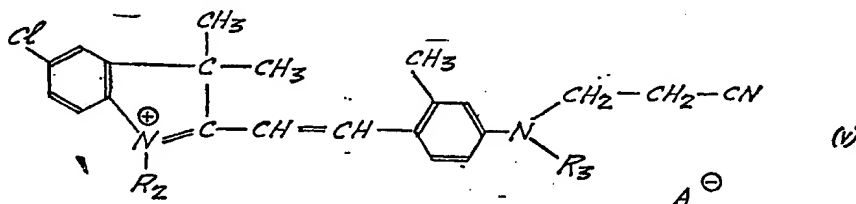
R₁ for a straight or branched alkyl radical which has at least two carbon atoms and may be substituted by a halogen atom,

R₂ for a methyl or ethyl radical and

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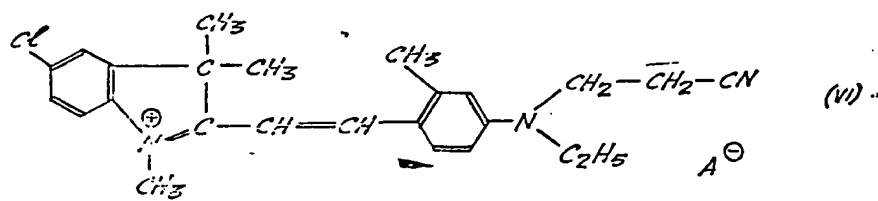
A[⊖] for an anion.

2. Styryl dyes according to Claim 1 and of the formula

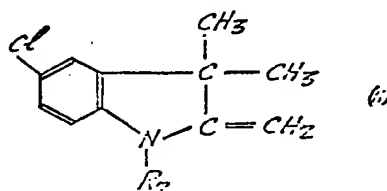


where R₂ is as defined in Claim 1 and R₃ stands for an ethyl propyl or butyl radical.

3. Styryl dyes according to Claim 1 and of the formula



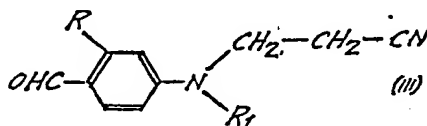
4. A process for the production of a styryl dye of the formula (I) according to Claim 1, which comprises reacting a compound of the formula



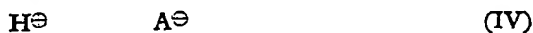
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where R_2 is as defined in Claim 1, with a compound of the formula

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where R and R_1 are as defined in Claim 1, and with an acid of the formula

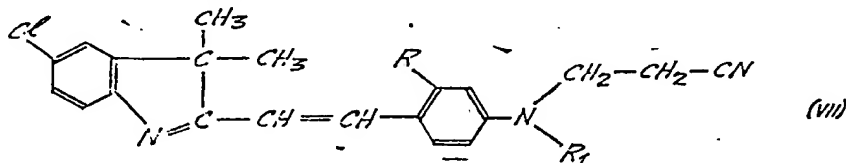


where A^- is as defined in Claim 1.

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5. A process for the production of a styryl dye of the formula (I) according to Claim 1, which comprises methylating or ethylating a compound of the formula

10



where R and R_1 are as defined in Claim 1.

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6. A process according to Claim 4, which includes the step of replacing the anion A^- in the dye of formula (I) by another anion.

15

7. An exhaust dyeing, pad dyeing or printing process in which polyacrylonitrile or acrylonitrile copolymer fibres or the component of such fibres in blend yarns or fabrics, or yarns or textiles made thereof, are exhaust dyed, pad dyed or printed with a dye of formula (I).

20

8. An exhaust dyeing, pad dyeing or printing process in which synthetic polyamide or synthetic polyester fibres which have been modified by the introduction of acid groups or the component of such fibres in blend yarns, or fabrics, or textiles made thereof, are exhaust dyed, pad dyed or printed with a dye of formula (I).

20

9. A dyeing process in which leather is dyed or printed or a plastics material is coloured with a dye of the formula (I) according to Claim 1.

25

10. A dyeing or printing process in which paper is dyed or printed with a dye of the formula (I) according to Claim 1.

25

11. Polyacrylonitrile and acrylonitrile copolymer fibres, blend yarns and fabrics containing such fibres, and textiles made thereof exhaust dyed, pad dyed or printed by a process according to Claim 7.

30

12. Synthetic polyamide or synthetic polyester fibres which have been modified by the introduction of acid groups, blend yarns and fabrics containing such fibres, and textiles made thereof, exhaust dyed, pad dyed or printed by a process according to claim 8.

30

13. Leather dyed or printed or plastics materials coloured by a process according to Claim 9.
14. Paper dyed or printed by a process according to Claim 10.
- 5 15. The particular dyes herein described and as illustrated in any of Examples 1 to 13. 5
16. A process for the production of a dye according to Claim 1 substantially as herein described in any one of Examples 1, 1a, and 2 to 13.
17. Dyes whenever prepared by the process according to any of Claims 4 to 6 and 16.
- 10 18. The dyeing process conducted substantially as described in the Dyeing Example. 10

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1973.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.